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# A REVISED UPPER LIMIT OF NO<sub>2</sub> IN THE MARTIAN ATMOSPHERE

by

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## UNPUBLISHED PRELIMINARY DATA

### ABSTRACT

Spectrographic evidence of NO<sub>2</sub> in the Martian atmosphere produced by Kiess, Karrer, and Kiess is interpreted as being inconclusive. On the contrary, high dispersion spectrograms of Mars have been analyzed and no identifications of NO<sub>2</sub> features were found. One such Martian and lunar spectrogram which shows solar lines as faint as 7.5 mÅ<sup>0</sup> equivalent width is combined with laboratory data on NO<sub>2</sub> to derive an upper limit of 0.1 mm-atm NO<sub>2</sub> in the Martian atmosphere. This is a factor of 10 lower than any previous estimate. The question of N<sub>2</sub>O<sub>4</sub> in the polar caps is re-examined in terms of this upper limit. It is found that only high local concentrations of NO<sub>2</sub> and N<sub>2</sub>O<sub>4</sub> near the Martian surface can explain the polar caps in this way. This conclusion probably would be incompatible with recent evidence of H<sub>2</sub>O on Mars, so the theory of nitrogen oxides contributing to Martian phenomena cannot be accepted unless conclusive spectroscopic evidence is found.

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## INTRODUCTION

Reports of evidence and the role of oxides of nitrogen in the Martian atmosphere have created considerable disagreement in the literature. A fundamental question which remains however is whether or not the oxides of nitrogen comprise a high enough concentration in the Martian atmosphere to account for any observed phenomena of Mars. If the answer is yes, it has been shown<sup>1,2</sup> that nearly all existing interpretations of Martian phenomena must be abandoned. This question is becoming increasingly significant at a time in which engineering models of the Martian atmosphere are being considered in preparation for the scientific exploration of the planet.

Of particular interest is the equilibrium mixture of nitrogen peroxide consisting of the dioxide  $\text{NO}_2$  and the tetroxide  $\text{N}_2\text{O}_4$ . Spectrograms taken by Kiess and Corliss<sup>3</sup> in 1956 and again in 1960-61 were found by the observers to contain features of  $\text{NO}_2$ . From these spectra Kiess, Karrer, and Kiess<sup>1</sup> proposed that many observed Martian phenomena can be explained uniquely by the chemical and physical properties of the oxides of nitrogen. Objections to their theory have been discussed by Huang<sup>4</sup> and Sinton<sup>5</sup>. Sinton calculated



an upper limit of 2.2 mm-atm  $\text{NO}_2$  in the Martian atmosphere from an infrared band at 3.43  $\mu$ . He concluded that this amount is "certainly insufficient to produce the observed Martian phenomena." A rebuttal by Kiess, Karrer, and Kiess<sup>2</sup> indicates that a concentration of 2.2 mm-atm is "not evidence against our theory, but in accord with what laboratory experiments indicate as sufficient to account for the color phenomena of Mars". Spinrad<sup>6</sup> has lowered the upper limit to 1 mm-atm by estimating the threshold of detection of  $\text{NO}_2$  on Martian spectrograms as compared to a large laboratory path of 10 cm-atm.

The results of this research are: (1) a discussion of my interpretation of Martian spectra obtained by Kiess et al; (2) setting an upper limit of 0.1 mm-atm  $\text{NO}_2$  in the Martian atmosphere, a factor of 22 lower than Sinton's upper limit and 10 lower than Spinrad's upper limit; and (3) using this result to re-examine the problem of  $\text{N}_2\text{O}_4$  in the polar caps.

#### COMMENTS ON THE EVIDENCE OF MARTIAN $\text{NO}_2$

A Martian spectrum on October 11-12, 1956, taken by Kiess et al<sup>2</sup> shows large differences between the Martian spectrum and lunar spectrum in the region  $\lambda\lambda$  6160 - 6280. On that evening a great yellow cloud was observed on the planet and was interpreted by the authors as an equilibrium shift from  $\text{N}_2\text{O}_4$  to the relatively opaque  $\text{NO}_2$ , corresponding to a temperature increase on Mars. On their Figure 1, reproduced as Figure 1 here, arrows are indicated at "wavelengths of absorption features measured on a spectrogram of  $\text{NO}_2$ ." The correlation between Martian absorption features and the arrow locations

seems to be quite good, but many other features of both "absorption" and "emission" appear randomly on the Martian tracing and are not present on the lunar tracing. These effects can perhaps be due to plate grain or difference of resolution between the two microphotometer tracings. Moreover, since the choice of the exact number and location of the arrows indicating absorption features from an  $\text{NO}_2$  spectrogram is necessarily subjective, it would appear preferable actually to show the spectrogram of  $\text{NO}_2$  or its microphotometer tracing. I therefore question the evidence presented on Figure 1.

Another problem in accepting the evidence of Kiess et al is the spectral region (longward of  $\lambda$  6160) in which the evidence is reported. It is well known that  $\text{NO}_2$  absorbs more strongly in the blue region of the visible spectrum. Dixon<sup>7</sup> has plotted the absorption coefficient,  $k$ , of  $\text{NO}_2$  against wavelength with a 40 Å spectrophotometer slit. His curve is smooth except for small sinusoidal variations and shows that absorption systematically decreases with increasing wavelength. The value of  $\log_{10} k$  between  $\lambda$  4400 and 4500 is -2.1; and at  $\lambda$  6200 it is -3.35, where  $k$  is measured in  $\text{mm Hg}^{-1} \times \text{cm}^{-1}$ . This means that absorption strength in the blue bands for a given concentration of  $\text{NO}_2$  is equivalent to absorption strength in bands around  $\lambda$  6200 for a new concentration which must be increased by a factor of 18. Of course, the fine structure afforded by higher dispersion reduces this factor of detection between the two spectral regions. But it is still more profitable to look for  $\text{NO}_2$  features in the blue. My high dispersion laboratory spectrograms have indicated that strong bands of  $\text{NO}_2$  at blue wavelengths do not appear at wavelengths above  $\lambda$  6000 even if the concentration is increased somewhat.

Furthermore, two spectrograms of Mars, kindly lent to me by Dr. Kiess, indicate no  $\text{NO}_2$  features. A systematic microphotometric scan of the visible spectrum from  $\lambda\lambda$  4140 to 6600 using plates P122 (December 30-31, 1960) and P188 (February 6, 1963) shows no differences between the Martian spectrum and the lunar spectrum which are correlated with the laboratory features of  $\text{NO}_2$ .

#### CALCULATION OF UPPER LIMIT OF $\text{NO}_2$

Spectrograms of Mars and the Moon have been taken by Spinrad at the Dominion Astrophysical Observatory 48" reflector with a dispersion of  $2.1 \text{ \AA}/\text{mm}$ , IIaO emulsion, and entrance slit width of  $45 \mu$  on September 15, 1962. The spectral region is  $\lambda\lambda$  4050 to 4650 with optimum density from  $\lambda\lambda$  4300 to 4500. Fortunately, three of the strongest  $\text{NO}_2$  bands in the visible spectrum<sup>8</sup> are centered in this region at  $\lambda\lambda$  4350, 4448, and 4480. A careful visual survey was made over the entire spectral region of the plates for absorption features present in the Martian spectrum which were not present in the lunar spectrum; the survey showed no differences. The survey was repeated meticulously in the vicinity of the  $\text{NO}_2$  absorptions near  $\lambda\lambda$  4350, 4448, and 4480, but the two spectra were identical. In the vicinity of these wavelengths faint solar lines were identified on both the Martian and lunar plates. Wavelengths and equivalent widths from the Utrecht Atlas of the Solar Spectrum (1940) are listed in Table 1. Figure 2 shows microphotometer tracings of these plates around  $4480 \text{ \AA}$ , the region of the strongest  $\text{NO}_2$  band in the visible spectrum<sup>8</sup>. The lunar and Martian tracings are essentially identical. From the visual survey and microphotometric

analyses, it is concluded that neither fine structure nor broad features of  $\text{NO}_2$  appear on the Martian spectrogram.

Laboratory spectrograms of  $\text{NO}_2$  under simulated Martian conditions have been taken by the author at the Georgetown Observatory during the past two years. A vacuum system was constructed for the purpose of preparing pure samples of nitrogen peroxide at a measured pressure and temperature. A sample was introduced into an evacuated absorption cell of one meter length. The temperature of each sample was about  $-10^\circ\text{C}$  and pressures of samples were graded from 0.3 mm Hg to 8 mm Hg. The dissociation of  $\text{N}_2\text{O}_4 \rightleftharpoons \text{NO}_2$  was about 80 to 90% for the lower range of pressures between 0.8 mm Hg and 0.3 mm Hg. Spectra were photographed with a 103aO emulsion, dispersion of  $5 \text{ \AA}/\text{mm}$ , and slit width of  $28 \mu$ . The purpose of these spectra was to simulate a Martian atmosphere of nitrogen peroxide in sunlight and blackbody simulator light at various pathlengths. The results indicated that at  $\lambda 4480$  and other bands in the blue, absorption by  $\text{NO}_2$  was well-defined at a laboratory pathlength of 0.8 mm-atm  $\text{NO}_2$  but barely detected at a laboratory pathlength of 0.35 mm-atm. The discussion can be illustrated by Figure 2, which shows the  $\lambda 4480$  band in blackbody simulator light at 3 pathlengths. Although these broad features are more difficult to discern on a solar spectrum than on a blackbody spectrum, it is obvious that if a continuum were drawn along both the Martian and lunar spectra on Figure 2, the difference (Mars - Moon) would be negligible and certainly less than the  $\text{NO}_2$  pathlength 0.35 mm-atm. In terms of Martian abundance<sup>7, 9</sup> these figures are divided by a factor of at least 3.6 because of the oblique average path in and out of the Martian atmosphere. The result is that  $\text{NO}_2$  absorption features on

Mars would be easily detected at 0.22 mm-atm and marginally detected at 0.1 mm-atm. However, since the laboratory spectrograms have less than one-half the dispersion and coarser grain (but slightly narrower slit), the threshold of detection of the laboratory plates is not as good as the Victoria plates. Thus the upper limit of 0.1 mm-atm can be enforced with more than marginal certainty.

As mentioned by Spinrad<sup>6</sup>, the Doppler and Lorentz line widths in the laboratory and on Mars are probably unchanged, so pressure differences and saturation effects are neglected. The laboratory spectrograms were taken at a temperature of  $-10^{\circ}\text{C}$ , which is barely 10% higher than the expected mean Martian temperature. Also the electronic structure of  $\text{NO}_2$  near the band centers under consideration will not be noticeably changed for the lower temperatures expected on Mars.

It is interesting to note that an upper limit of 0.1 mm-atm  $\text{NO}_2$  in the Martian atmosphere corresponds to a fractional concentration of about 6 parts per hundred million. This value is somewhat less than that found in a heavy Los Angeles smog.

### $\text{N}_2\text{O}_4$ IN THE POLAR CAPS

At this point, the question of  $\text{N}_2\text{O}_4$  comprising the polar caps should be re-examined. The concentration of  $\text{NO}_2$  in the atmosphere at any given time would depend upon its equilibrium with the dimer  $\text{N}_2\text{O}_4$ . Lower temperatures and higher partial pressures of the equilibrium mixture favor the formation of  $\text{N}_2\text{O}_4$  so that only in the polar regions would the equilibrium shift to  $\text{N}_2\text{O}_4$ , which would become a chalky-white solid at very low temperatures to form the polar caps.

Otherwise, the equilibrium strongly favors  $\text{NO}_2$  at temperatures expected over most of the planet. Kiess et al<sup>2</sup> investigated both the vapor pressure data<sup>10</sup> and equilibrium data<sup>11</sup> at the lowest probable Martian temperatures. They found, for example, at a temperature of  $170^\circ\text{K}$  and vapor pressure of the oxide complex of 0.0015 mm Hg, that gaseous  $\text{N}_2\text{O}_4$  becomes solid, the dissociation  $\text{N}_2\text{O}_4 \rightleftharpoons \text{NO}_2$  is 2.3%, the partial pressure of  $\text{NO}_2$  is thus  $0.7 \times 10^{-4}$  mm Hg, and this is enough to produce an abundance of 1.8 mm-atm which is within Sinton's upper limit.

It is interesting to apply my upper limit to these data to determine: (1) the highest temperature at which  $\text{N}_2\text{O}_4$  can become solid in the polar regions and (2) the upper limit of  $\text{N}_2\text{O}_4$  as a function of temperature. This can be done easily by plotting partial pressure of  $\text{N}_2\text{O}_4$  against temperature for two partial pressures of  $\text{NO}_2$ : one at  $0.7 \times 10^{-4}$  mm Hg corresponding to an abundance of 1.8 mm-atm in accordance with Sinton's upper limit; and the other at  $4 \times 10^{-6}$  mm Hg corresponding to my upper limit of 0.1 mm-atm. Figure 3 shows that temperatures of the polar caps must be colder than  $156^\circ\text{K}$ , an unlikely low value. The only other way to explain the polar caps by  $\text{N}_2\text{O}_4$  would be to assume high local concentrations of nitrogen peroxide just above the caps, with trace concentrations over the rest of the planet. Admittedly the discussion has neglected such considerations. However, the entire approach appears uncomfortable when spectrographic evidence<sup>9</sup> of water vapor in the Martian atmosphere and previous work<sup>12</sup> can explain more directly the polar caps as being ice and hoar-frost. Recent spectrographic observations by Spinrad<sup>13</sup> further corroborate  $\text{H}_2\text{O}$  in the polar caps. He has reported an enrichment of water vapor in the vicinity of the melting polar cap. Moreover, water vapor combines very rapidly with nitrogen oxides,



so their co-existence would be difficult to explain.

Upper limits of  $N_2O_4$  in mm-atm for a mixed atmosphere are plotted as ordinates on the right side of Figure 2. It is interesting to note that the  $N_2O_4$  upper limit is very sensitive to temperature changes.

### CONCLUDING REMARKS

The upper limit determined herein is based upon only one observation of Mars. On the other hand, Spinrad's<sup>6</sup> upper limit was based upon several other spectrograms of good quality. My laboratory results applied to his lack of evidence on these other plates would imply upper limits of the order of my value.

From this discussion, it is apparent that unequivocal evidence of  $NO_2$  features in Martian spectrograms and derivation of  $NO_2$  concentration in future observations are necessary before a theory of nitrogen oxides can be accepted. Future observations at a Coude' spectrograph and a large telescope in the blue region of the spectrum would provide better spectral resolution and superior spacial resolution on the planetary disc. According to Kiess et al<sup>2</sup>, one would expect to find  $NO_2$  preferentially at the lower and warmer dark areas and above the warmest polar sources of the system. These areas should be isolated in any future observations.

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| WAVELENGTH REGION<br>OF NO <sub>2</sub> BAND | WAVELENGTH OF<br>FAINT SOLAR LINE            | EQUIVALENT WIDTH OF<br>FAINT SOLAR LINE |
|--|--|---|
| λ 4350                                       | λ 4350.251<br>4350.585                       | 28 mA<br>36                             |
| 4448   | 4445.681<br>4446.403<br>4447.356             | 7.5<br>8.5<br>11                        |
| 4480   | 4478.025<br>4478.322<br>4478.628<br>4479.387 | 15<br>10<br>12<br>18                    |

**TABLE 1.** Wavelengths and equivalent widths of faint solar lines identified on Victoria, B. C. (September 15, 1962) Martian and lunar spectrograms V349 and V345.

## Figure Captions

Figure 1. Evidence of  $\text{NO}_2$  in the Martian atmosphere as presented by Kiess, Karrer, and Kiess,<sup>2</sup> October 12, 1956. Arrows mark the wavelengths of absorption features measured on a spectrogram of  $\text{NO}_2$ .

Figure 2. Lack of evidence of  $\text{NO}_2$  in the Martian atmosphere is illustrated by microphotometer tracings of Martian and lunar spectrograms V349 and V345 taken by Spinrad on Sept. 15, 1962. Plots of my laboratory absorption spectrograms at three  $\text{NO}_2$  pathlengths indicate thresholds of detection of  $\text{NO}_2$ . The region chosen is  $\lambda$  4480 which is the strongest  $\text{NO}_2$  band in the visible spectrum.<sup>8</sup> Zero points are not shown, but the ordinates are linear in per cent transmission for each spectrum. The Martian and lunar spectra are reduced ( $\times 3.7$ ), but the original tracings reveal no  $\text{NO}_2$  absorption around  $\lambda$  4480 for the Martian spectrogram.

Figure 3. Partial pressure ( $\text{N}_2\text{O}_4$ ) vs. temperature, given a partial pressure ( $\text{NO}_2$ ). Assuming a mixed Martian atmosphere: Curve (A) corresponds to a partial pressure ( $\text{NO}_2$ ) of  $0.7 \times 10^{-4}$  mm Hg, or 1.8 mm-atm ( $\text{NO}_2$ ), within Sinton's upper limit of 2.2 mm-atm; Curve (B) corresponds to a partial pressure ( $\text{NO}_2$ ) of  $4 \times 10^{-6}$  mm Hg, or 0.1 mm-atm ( $\text{NO}_2$ ), the value of my upper limit. The vapor pressure curve of  $\text{N}_2\text{O}_4$  is included to demonstrate that polar caps must be colder than  $156^\circ\text{K}$ . The ordinate on the right side indicates the upper limit of  $\text{N}_2\text{O}_4$  in mm-atm as a function of temperature for curves (A) and (B).

